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Recent advances in tandem selenocyclization and tellurocyclization with alkenes and alkynes

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Seleno-containing heterocycles exist widely in pharmaceutical molecules and the skeletons of natural products. The addition of organoselenium to alkenes and alkynes *via* intramolecular tandem selenocyclization is an efficient method for preparing selenofunctionalized heterocycles. In this protocol, multiple bonds are formed in a single reaction without the need to isolate intermediates. This review highlights recent progress in this rapidly growing area with an emphasis on the scopes, limitations and the mechanisms of these different reactions. Besides, tandem tellurocyclization with alkenes and alkynes is also briefly discussed.

1. Introduction

Organoselenium compounds are considered an important class of molecules in organic synthesis. These compounds are widely applied in materials and catalysis and as intermediates in organic synthesis.¹ In addition, organoselenium compounds have been shown to have pharmacological activities such as anticonvulsant, antioxidant, antidepressant, anticancer, antitumor, anti-inflammatory and antiviral properties.² The introduction of a selenium atom into a potentially bioactive molecule can dramatically increase the native biological activity of the substrate. Meanwhile, heterocycles, which exist in natural products and biologically active molecules, play sig-

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 ^bSchool School of Chemistry and Materials Science, Liaoning Shihua University, Dandong Road 1, Fushun 113001, P. R. China. E-mail: lilei0814.com@163.com nificant roles in the pharmaceutical and agrochemical industries.³ For all these reasons, continuous research effort has been devoted to the development of useful methods for synthesizing selenofunctionalized heterocycles. Currently, one way to access these compounds is the direct functionalization of the heterocycle precursor with a selenium source *via* transition metal catalysis.⁴ However, this method is limited by its poor regioselectivity and direct use of preformed or commercially available heteroaromatic counterparts. Alternatively, the addition of organoselenium to alkenes and alkynes *via* intramolecular tandem selenocyclization is an efficient protocol for preparing selenofunctionalized heterocycles. In this protocol, multiple bonds are formed in a single reaction without the need to isolate intermediates.

Over the past decade years, the selenocylization of the selenium electrophiles (*e.g.*, ArSeCl, ArPhBr, and ArthSe) with alkenes or alkynes have been deeply developed.⁵ However, the sensitivity to moisture and a short shelf life limited the appli-



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cation. In contrast, diselenides are easily accessible and operable selenium reagents in organic synthesis, making them a good choice for selenocyclization.⁶ Although some approaches have been reported for the intramolecular tandem selenocyclization reactions of diorganyl diselenides with alkenes and alkynes, few efforts have systematically reviewed tandem selenocyclization with alkenes and alkynes. In consideration of recent research progress and to better understand seleniumbased intramolecular tandem selenocyclization, this review article firstly introduce the traditional selenocylization with some selenium electrophiles, and then summarize the latest contributions to selenocyclization reactions of diorganyl diselenides with alkenes and alkynes between 2010 and 2020 and highlights the insights gained from previous methodological and mechanistic studies. The content is categorized by the type of catalysis, including metal catalysis, visible-light catalysis, electrochemical catalysis, organocatalysis, and other catalysis types involving hypervalent iodine- and peroxide-promoted reactions.

2. Traditional selenocyclization

Since the discovery in the late 1960s that species of type RSeX added stereospecifically to simple alkenes to the formation of a selenolactone,⁷ these reactions were extensively developed construct the selenofunctionalized heterocycles. to Mechanistically, seleniranium ion 2 was formed by the addition of RSeX to unsaturation bond, which then was captured by a pendant nucleophilic group to generate a cyclic product with chemo-, regio-, stereo-specificity (Scheme 1).8 For example, in 2013, the group of Shaw reported tandem monocyclization and bicyclization reactions between alkenes and PhSeCl in the presence of catalytic quantities of $Sc(OTf)_3$ to access polysubstituted tetrahydroquinoline 6 and octahydrophenanthridine 8 in moderate to high yields (Scheme 2).9 In this process, two rings, three bonds, and three stereogenic centers were formed with excellent stereo- and regio-control in one step.



Scheme 1 Mechanism of traditional selenocyclization.



Scheme 2 PhSeCl promoted synthesis of selenyl tetrahydroquinoline and octahydrophenanthridine.

Moreover, *N*-(2-nitrophenylselenenyl)succinimide (NPSP) was also used as the electrophilic selenium source. In 2015, Yeung and co-workers described an enantioselective selenolactonization of olefinic acids **9** and NPSP, using hydroquinidine 1,4-phthalazinediyl diether ((DHQD)₂PHAL) as the catalyst (Scheme 3).¹⁰ A series of functional groups were tolerant with this catalytic system, giving the corresponding selenolactones **10** with good yields and ee values. Additionally, heteroaromatic substrate was also reacted well in this catalytic system.



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Scheme 3 NPSP promoted synthesis of enantioselective selenolactonization.



Although cyclohexyl substrate was accommodated in 89% yield, the ee was only 16% under this catalytic protocol. The mechanism study shows that the large catalyst pocket was required for this transformation to avoid racemization of the chiral episeleniranium ion, introducing high enantioselectivity.

Allenes owing to two cumulative carbon–carbon double bonds have some unique chemical properties.¹¹ For example, in 2004, the Ma's group demonstrated a electrophilic cyclization of 2,3-allenoic acids **11** with PhSeCl for the synthesis of β -organoselenium butenolides **12** (Scheme 4).¹² The reaction showed a broad substrate scope, and 4-mono-substituted, 2,4disubstituted, and 2,4,4-trisubstituted 2,3-allenoic acids can all be applied to afford the corresponding products in 77–98% yields. Moreover, this protocol can also be compatible to the corresponding electrophilic cyclization of PhSCl.

In 2012, Alcaide and co-workers disclosed an electrophilic selenocyclization of 2-indolinone-tethered allenols **13** with various selenenylating reagents, affording different heterocycles, which was shown good chemoselectivity (Scheme 5).¹³ PhSeBr, *N*-phenylselenosuccinimide (NPSS), or diphenyl diselenide as donors of PhSe⁺ in reactions with 2-indolinone-tethered allenol XX delivered spirocyclic selenolactams **14**, and



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double bond produces the intermediate **16**. The intermediate **16** has two regioisomer: **16-I** and **16-II**, which occur a ring expansion to give the corresponding products **15** and **17**. The migration of the phenyl group is preferred to the migration of the carbonyl one, and **15** is the major product. In subsequent work, Alcaide and coworkers reported a

HO

13

PhS

16-

PhSeBr

CH₂Cl₂, rt

 R^1 , R^2 = Methyl

0

è2

In subsequent work, Alcaide and coworkers reported a metal-free oxidative selenofunctionalized reaction between allenes and diphenyl diselenide (Scheme 6).¹⁴ This reaction



Scheme 6 The synthesis of α -seleno- α , β -unsaturated carbonyls and selenated furan.

Dha

 \dot{R}^2

15, 46-89 %

R²

PhSe

PTSA (15 mol %)

CH₂Cl₂, rt

R¹ = Aryl, alkyl

R² = Methyl, ⊢

СНО

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employed 1-fluoropyridinium compounds oxidative as functionalization reagents to access two types of α-seleno- α , β -unsaturated carbonyls (α-selenoenals 19 and α -selencence 20) by changing the substituents at the allene end. In the case of allenone as a substrate, the α -selenoenone was failed to obtained, and the cyclized selenated furan 22 was afforded in 63% yield. The protocol disclosed the oxidation of (PhSe)₂ promoted by 1-fluoropyridinium triflate to generate the electrophilic species PhSe(OTf).

3. Diorganyl diselenides promoted selenocyclization

3.1 Transition metal-catalyzed selenocyclization

3.1.1 Iron(m)-promoted selenocyclization. Over the past decade, iron salts have appeared as alternative and promising catalysts for a wide range of organic transformations¹⁵ due to their low cost, good stability, abundance, ease of handling, and excellent tolerance toward various functional groups.¹⁶ The use of catalytic and stoichiometric quantities of iron(m) salts is a particularly efficient strategy to promote the selenocyclization of diselenides with alkenes or alkynes. Fundamentally, iron(m) salts act as Lewis acids and coordinate with selenium, which enhances the polarization of the diselenide bonds and facilitates electrophilic alkene selenocyclization with nucleophiles.

The group of Zeni reported a series of iron(m)-promoted cyclization of alkynes and diselenides. This strategy provides a new approach to obtain various selenofunctionalized heterocycles such as benzo[*b*]furans chromenones, indoles, isoxazoles, benzoxazines, dihydrofurans, isochromenimines, naphthalenes from readily accessible starting materials under mild conditions with efficiency and operability (Scheme 7).¹⁷ The authors proposed the mechanism that the key of these selenocyclizations are the iron-seleno complex generated from the reaction of FeCl₃ and diorganyl diselenide (RSe)₂. The electrophilic portion of the selenium species coordinates to the triple carbon–carbon bond to generate the seleniranium ion



Scheme 7 Iron(III)-promoted selenocyclization of alkynes.

26. The cyclized cationic intermediate **27** is then generated *via* intramolecular nucleophilic attack. Finally, deprotonation of **27** gives the selenocyclized product **24**.

In 2020, the group of Ji established an iron(m) chloride-promoted cyclization between α , β -alkynic tosylhydrazones **28** and diselenides (Scheme 8).¹⁸ The reaction proceeded efficiently in the presence of 1.0 equiv. FeCl₃ in 1,2-dichloroethane (DCE) at room temperature, providing a series of 4-(arylselanyl)-1*H*-pyrazoles **29** with good functional group tolerance. Meanwhile, Koketsu *et al.* reported seleno-cyclization of alkyne **30** and diselenides, furnishing a series of 6*H*-isoquinolino[2,1-*a*]quinazolin-6-one **31** (Scheme 9).¹⁹ In this reaction, C–N and C–Se were constructed in one step using 1.5 equivalent of FeCl₃·6H₂O in dichloromethane at room temperature. The plausible mechanisms of these two reactions are similar to above mentioned.

3.1.2 Copper catalyzed selenocyclization. Copper salts can act as catalytic cross-coupling agents, Lewis acids, and oxidizing agents in organic synthesis with the relatively low cost of copper and the realization of catalysis in many instances.²⁰ Among them, copper-facilitated selenocyclization reactions between the diselenides and alkenes or alkynes have been widely applied as one of the most powerful tools for the synthesizing of seleno-heterocycle. For example, in 2017, Zeni and coworkers accomplished copper catalyzed cyclization of propargyl pyridines 32 with diorganyl diselenides (Scheme 10).²¹ The reaction was catalyzed by 20 mol% of CuI with 2 equiv. Na₂CO₃ as a base in DMF at 60 °C. A variety of propargyl pyridines and diorganyl diselenides were screened, and a wide range of 2-(organoselenyl)-indolizine 33 were obtained in generally good yields. Notably, when propargyl pyridines was equipped with a terminal alkyne, the indolizine with two phenyl selenium groups in the structure (34) was obtained in 30% yield. However, employing dibutyl diselenide as organoselenium source, the desired product was not



Scheme 8 Iron(III)-promoted synthesis of selenyl pyrazoles.



Scheme 9 Iron((0))-promoted synthesis of selenyl isoquinolino[2,1-a] quinazolin-6-one.



Scheme 10 Cul-catalyzed synthesis of selenyl indolizine.



Scheme 12 Cul-catalyzed synthesis of selenylated benzo[b]furan.

detected, and the corresponding 2-hydrogenated indolizine **35** was obtained *via* beta-selenoxide elimination.

To get insight the mechanism aspect of this cyclization, some control experiments were performed. These experiments revealed that the copper-selenolate species **36** generated by mutual action between copper(1) iodide and diorganyl diselenide was essential for the reaction. In the mechanism (Scheme 11), an intermediate **37**, as an electrophile through the activation by coordination of the Cu(1) ion to the alkyne, is formed. Intermediate **37** is then converted into **38** *via* intramolecular nucleophilic attack of N atom. Deprotonation then produces the 2-copper-indolizine **39**. The subsequent reductive elimination of copper leads to the formation of the final product **33**.

A similar transformation was achieved by Godoi.²² The selenocyclization between 2-alkynylphenols and diorganyl diselenides enabled selenocyclization provided 3-organoselanylbenzo[b]furan derivatives in moderate to good yields (Scheme 12). In contrast to the Zeni's work,²¹ this reaction did not need any base and worked smoothly in DMSO at room temperature by promotion of 1.5 equiv. CuI. The protocol performed excellent functionality tolerance. 2-Alkynylphenol, containing electron-donating groups, electron-withdrawing groups and halogen groups were all tolerated. Moreover, naphthylsubstituted alkyne also reacted well in this catalytic system. In particular, low reactive aliphatic alkyne was accommodated with moderate yields. Moreover, the dialkyl diselenides was proven to be applicable in this reaction.

Notably, 3-organoselanylbenzo[b]furan could be used to prepare for different functionalized benzo[b]furans, demonstrating the synthetic applicability of this protocol.

In 2018, Zhong and co-workers developed a copper-catalyzed tandem selenoamination reaction of alkenes, successfully affording a series of seleno-N-heterocycles (*e.g.*, indoline, tetrahydroquinoline, pyrroline, and piperidine derivatives) with 73–93% yields (Scheme 13).²³ In this approach, 10 mol% of CuBr₂ was utilized in DMSO at 120 °C in air. During the mechanistic investigation, oxygen and DMSO as co-oxidants were necessary for this transformation. Moreover, radical quenching experiments suggested a radical mechanism is not likely the case in the present catalytic system. As shown in Scheme 13, the Se–Se of diselenide could be polarized by CuBr₂ to access the coordination 44, which undergoes an electrophilic addition to the olefin moiety of 42. The intramolecular nucleophilic attack by nitrogen and deprotonation then furnish the desired product 43 and selenophenol.



Scheme 11 Proposed mechanism of Cul-catalyzed synthesis of selenyl indolizine.



Scheme 13 CuBr₂-promoted synthesis of selenylated N-heterocycle.

Selenophenol is oxidized to diselenide by O_2 and DMSO, and re-enter to the catalytic cycle.

Soon after, Reddy's group reported a CuCl₂-catalyzed synthesis of selenyl nicotinates from enynyl azide **45** with diorganyl diselenides (Scheme 14).²⁴ The enynyl azide bearing aryl groups with different electron-donating or electron-withdrawing groups and 2-thienyl all underwent this transformation smoothly, leading to desired 5-selenyl nicotinates **46** with yields ranging from 78–98%. It is worth noting that aryl-substituted, heterocyclic, and alkyl-substituted diselenides are also compatible to this reaction. The mechanism for this intramolecular selenoamination is similar to that described in Zhong's work.²³

In 2018, Xu and co-workers demonstrated a selenocyclization of 2,3-allenoic acids 47 with diselenides in the combination of CuCl and $(NH_4)_2S_2O_8$ as catalytic oxidation system (Scheme 15).²⁵ The reaction enabled sulfenylation/cyclization and subsequent oxidation to provide selenylated butenolides **48** in 63–82% yields. $(NH_4)_2S_2O_8$ played dual roles as a radical initiator as well as oxidant. Moreover, selenylated butenolides could be applied for synthesis of the corresponding furan derivatives.

The proposed mechanism by the authors was depicted in Scheme 16. First, a selenyl radical is formed *via* the homolysis of RSeSeR in the presence of $(NH_4)_2S_2O_8$. The addition of selenyl radical to 2,3-allenoic acids gives the radical intermediate **49**. The further oxidation of intermediate **49** by Cu(II) affords the intermediate **50**. Finally, the intramolecular attack of intermediate **50** leads to the cyclized products **51**. Another pathway is also proposed. Cu(II) coordinated to 2,3-allenoic acids, generating the complex **51**. Then, the addition of selenyl radical to **51** gives Cu(III) intermediate **52**. Finally, reductive elimination is occurred to release the desired product **48**.



(R¹Se)₂ (1.5 equiv)

CO_oMe

Scheme 14 CuCl₂-catalyzed synthesis of selenyl nicotinates.



Scheme 15 CuCl₂-catalyzed synthesis of selenylated butenolides.



Scheme 16 Proposed mechanism CuCl₂-catalyzed synthesis of selenylated butenolides.

Organofluorine compounds constitute an attractive class of compounds that have attracted significant attention from researchers in a variety of disciplines. In 2019, the group of Sun successfully synthesized a series of 4-seleno-substituted α,α -difluoro- γ -lactams 54 using *N*-allyl-2-bromo-2,2-difluoro-acetamides 53 and diorganyl diselenides catalyzed by 10 mol% CuI in DCE at 120 °C under external-oxidant-free conditions (Scheme 17).²⁶ Various *N*-aryl-substituents of bromodifluoroacetamides with different electron-donating or electron-with-drawing groups undergo this transformation smoothly, leading to desired products with yields ranging from 63–82%. Notably, *N*-alkyl-substituted bromodifluoroacetamide could proceed well in this reaction. Furthermore, diphenyl diselenides, 1,2-di(thiophen-2-yl)diselane and dimethyldiselenide were also compatible to this reaction.

Regarding the mechanism, control experiments and radical quenching experiments demonstrated this process proceeded through a radical pathway. The authors proposed the following possible reaction mechanism (Scheme 18).



Scheme 17 Cull-catalyzed synthesis of 4-seleno-substit α, α -difluoro- γ -lactams.

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A single-electrontransfer (SET) between Cu(i) and 53 occurs to afford a Cu(ii) species and radical intermediate 55. Next, the addition of the fluoroalkyl radical to the unsaturated double bond affords alkyl radical intermediate 56 *via* a 5-*exo-trig* cyclization. The alkyl radical intermediate 56 reacts with diphenyl diselenide to form the desired product 54 and selenyl radical, which further reduces Cu(ii) to Cu(i) and selenyl anion (PhSeX) to complete the catalytic system.

3.2 Visible light-promoted selenocyclization

Recently, photoredox catalysis has emerged as a useful tool for radical reactions *via* visible light-induced processes. Compared with previous methods, photoredox catalysis is inexpensive and has the advantages of environmentally-benign (it does not require excess amounts of transition metals or oxidants), high efficiency and easy to use.²⁷ Notably, diselenide bonds possess a lower bond energy (172 kJ mol⁻¹), which could facilitate the generation a selenium radical species *via* the homolytic cleavage of the Se–Se single bond under visible-light irradiation without any photocatalyst. Therefore, the construction C–Se to synthesize selenofunctionalized heterocycles under visible-light irradiation has become more appealing.

In 2013, Ragains and co-workers reported a visible lightpromoted selenocyclization of alkenes at room temperature (Scheme 19).²⁸ In this reaction, bench-stable PhSeSePh is combined with CBr₄ under the irradiation of a 5 W blue light-emitting diode (LED), resulting in the in situ generation of reactive PhSeBr. This reaction showed a broad substrate scope, generating O-heterocycles in high yields along with N-heterocycles in moderate to high yields. Notably, diphenyl ditelluride was successfully suitable for this strategy to afford the tellurofunctionalization products in 53-75% yields in dichloromethane as solvent. To further demonstrate the application of this method, the Amaryllidaceae alkaloid y-lycorane was synthesized. Mechanistic studies and DFT calculation suggested visible light irradiation promoted the phenylselenyl radical abstraction of bromine from CBr₄ to generate phenylselenyl bromide in situ. The detailed mechanism of these reactions is still under investigation.

Later, the group of Liu developed a visible light-driven selenocyclization of N-allylamides in MeCN in the presence of



Scheme 19 Visible light-promoted synthesis of β -selenyl O-heterocycles and N-heterocycles.

2 mol% 4CzIPN under visible-light and in air (Scheme 20).29 While dihydroisoxazole was produced in 73% yield without any photocatalyst under these optimized reaction conditions, the use of 4CzIPN as a photocatalyst promoted the reaction process. In contrast to other seleno cylization reactions, this protocol only needed 60 mol% diselenides. In addition, many substituted the allylic amides and various diselenides were well tolerated in this transformation and gave the corresponding products 60 in good to excellent yields. Inspired by this result, a series of heterocycles were prepared by investigating the scope of the nucleophilic reagent, generating the corresponding products 62 in 51-98% yields. A possible reaction mechanism (Scheme 20) was proposed based on fluorescence quenching experiments. In this mechanism, the ground state 4CzIPN is excited to *4CzIPN under visible light irradiation. The excited state then undergoes a SET reaction



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with diphenyl diselenide to generate $(PhSe)_2^{*+}$ radical cation and $4CzIPN^{*-}$ radical anion. Then, the molecular oxygen oxidized $4CzIPN^{*-}$ to the ground state completes the photoredox cycle. Meanwhile, the addition of diselane radical cation $(PhSe)_2^{*+}$ to *N*-alkenylamide **59** produces seleniranium cation **63**, which undergoes intramolecular nucleophilic cyclization to obtain the desired product **60**.

In 2017, an efficient approach for the preparation of selenium substituted spiro[4,5]trienones based on visible lightinduced selenium radical-cyclization of N-aryl alkynamides 64 under oxygen atmosphere at room temperature without external photocatalyst was described for Baidya and coworkers (Scheme 21).³⁰ This reaction showed a wide range of functional groups tolerances. Diverse N-aryl alkynamide and diaryl diselenides bearing electron-donating as well as electron-withdrawing groups in aryl ring can achieve the products 65 in moderate to excellent yields. In addition, good yields were achieved in gram-scale reactions. A spiro-ring-opening strategy was realized to give fully substituted acryl amides 66. Based on several control experiments, a possible radical pathway mechanism was proposed. First, under visible light irradiation, the addition of selenyl radical produced via homolytic cleavage of the Se-Se single bond to the triple bond produces a vinyl radical 67. Subsequently, intramolecular radical ipso-cyclization affords 68. Oxidative dearomatization would then occurs under oxygen atmosphere and in the presence of diaryl diselenide to afford the desired product.

In 2017, the group of Wang developed a facile route to prepare 3-selenylindoles from *N*-(2-(ethynyl)aryl)benzenesulfonamide **70** and diaryl diselenides under 3 W blue LED irradiation (Scheme 22).³¹ The authors optimized reaction conditions and found that H_2O_2 (30% aqueous solution) as oxidant was necessary for this transformation. Moreover, this methodology exhibited good functional group tolerance, giving rise to the 3-selenylindoles **71** in moderate to excellent yields. With the result of radical-trapping experiment, a radical free mechanism was proposed. Initially, hydroxyl radical generates from the homolytic cleavage of H_2O_2 under blue LED irradiation. Then a single electron transfer between **70** and hydroxyl radical gives the intermediate **72**. After the intra-

65, 42-92 %

intramolcular

66.81-94 %

02

ArSeSeA



Scheme 22 Visible light-promoted synthesis of 3-selenylindoles.

molecular cyclization and deprotonation, radical intermediate 74 is formed. Finally, the reaction between diphenyl diselenide and 74 leads the desired product 71 and phenylselenyl free radical. The phenylselenyl free radical further reacts with 74, delivering the final product.

In 2019, Xu and coworkers reported a Se radical-triggered multi-component tandem cyclization of alkyne-tethered cyclohexadienones 75 and diaryl diselenides under the irradiation of 25 W white LEDs at 40 °C temperature (Scheme 23).³² This reaction gave 5-hydroxy-3-selenyl-4a,8a-dihydro-2H-chromen-6 (5*H*)-ones **76** in 40–88% yields in the presence of 2 equiv. H_2O and CsOAc in chlorobenzene at 40 °C. Moreover, the reaction could be performed in the absence of a base in dry toluene at 60 °C, producing 3,5-diselenyl-4a,8a-dihydro-2H-chromen-6 (5H)-ones 77 in 62-81% yields. These results demonstrate water is crucial for this transformation. To gain more insight into the effect of water, some control experiments were performed. First, decreasing the amount of H₂O to 1 equiv. provided 76 in 40% yield and 77 in 30% yield. Next, 77 was converted to the desired product 76 under the standard conditions indicating that 77 is a possible intermediate. ¹⁸O-Labelling experiments showed that the oxygen atom of the hydroxyl group originated from water. Moreover, a radical-trapping experiment using 2,2,6,6-tetramethylpiperidine-1-oxyl



Scheme 21 Visible light-promoted synthesis of spiro[4,5]trienones.

(ArSe)₂ (2.0 equiv.) blue LED, MeCN, rt O₂ balloon

R¹ = Alkyl; R² = Alkyl, Het(Aryl)

 $R^3 = EWG, EDG$

64



Scheme 23 Visible light-promoted synthesis of selenyl chromenones.

(TEMPO) was performed to probe the possibility of a radical mechanism in this transformation.

Through a series of experimental observations and surveys of previous literature, they proposed the following possible reaction mechanism (Scheme 24). First, under visible-light irradiation, phenylselenyl free radical generated from diphenyl diselenide undergoes a radical addition to substrate 75 to produce alkenyl radical 78. Subsequently, intramolecular radical cyclization gives intermediate 79, which is trapped by another phenylselenyl free radical to deliver the product 77. In the presence of CsOAc, nucleophilic substitution occurs with water and 77, leading to the desired product 76. Interestingly, some products showed potent inhibition activities against cancer cell growth *in vitro*.

In 2020, Xu and coworkers further developed visible lightinduced selenocyclization reaction of indolyl-ynones **80** with diselenides at room temperature under air atmosphere (Scheme 25).³³ Diverse 3-selenospiroindolenines bearing various functional groups were obtained in moderate to good yields. Similarly, phenylselenyl free radical is generated from diphenyl diselenide under visible-light irradiation. The desired product is then obtained through the radical addition/oxidation/deprotonation pathway. Compounds **81a** and **81b** were



Scheme 24 Proposed mechanism of visible light-promoted synthesis of selenyl chromenones.



3-selenospiroindolenines.

d synt

of

tested for *in vitro* anticancer activity by MTT assay and showed potent inhibitory activity against cancer cell growth.

Very recently, the group of Wang disclosed a regio- and chemoselective radical cascade cyclization of 1,6-enynes 82 and areneselenosulfonates 83a under 34 W blue LED irradiation in the air without any photocatalysts (Scheme 26).³⁴ Numerous substrates (82) were examined, and the corresponding cyclized products (84) were obtained in good to excellent yields. This reaction also proceeded smoothly using diaryl diselenides 83b with 1,6-envnes, and observed desired products with moderated to goods yields. However, this method was not applicable when the chain length was increased from one to two or three. The internal alkene and free amine in envne were also not tolerant for this transformation. This protocol offers an efficient approach to build selenium substituted pyrrolidine derivatives via multiple chemical bond constructions in 5-exo-dig fashion, including one C-S bond, one C-Se bond, and one C-C bond.

Notably, some control experiments indicated the reaction proceeded in a radical way, and the visible-light irradiation was necessary. The reactivity of the chalcogen group in the reaction was tested by the combination of 82a with 83a and 83b. The result suggested that tosyl radical was more reactivity than phenylselenyl, demonstrating the regio- and chemoselectivity. The proposed mechanism is described in Scheme 27. The tosyl (85) and phenylselenyl free radical (86) are generated by visible light irradiation. Tosyl radical 85 is added to 1,6-envnes 82a to generate alkyl radical intermediate radical 87. Then intramolecular 5-exo-dig cyclization gives rise to the corresponding vinyl radical 88, which is further trapped by phenylselenyl free radical (86) to generate desired product 84a. The reverse transformation products were not observed, probably due to the higher stability of the tertiary alkyl radical intermediate 87 compared to the vinyl generated by the tosyl



Scheme 26 Visible light-promoted synthesis of seleno-containing pyrrolidine.

Control experiment



Scheme 27 Control experiments and proposed mechanism of visible light-promoted synthesis of seleno-containing pyrrolidine.

radical addition to alkyne. This protocol showed excellent regio- and chemoselectivity, good functional tolerance.

3.3 Electrochemically enabled selenocyclization

In the past few years, electrochemistry has been recognized as one of the most powerful and sustainable methods in organic chemistry since electrochemical methods avoid chemical oxidants, reductants, and transition-metal catalysts.³⁵ Compared to traditional chemical synthetic methods, electrochemically induced selenocyclization methods for the difunctionalization of alkenes and alkyne are relatively rare. More selenocyclization reactions for the synthesis selenyl heterocycles should be developed.

In 2019, Guo and co-workers reported an electrochemically induced oxidative cyclization of alkynoates or alkynamides with diselenides by using ${}^{n}Bu_{4}NPF_{6}$ as supporting electrolyte (Scheme 28).³⁶ In the cases of diselenides with aryl groups or alkyl groups, the reaction proceeded smoothly, giving the corresponding coumarins or quinolinones **90** in moderate to good yields. This protocol also demonstrated a broad substrate scope of alkynoates and alkynamides, except when *para*-OMe



Scheme 28 Electrochemically induced synthesis of selenated coumarins and quinolinones.

was substituted on the aryl group. However, terminal alkyne was ineffective for this transformation. Moreover, the reaction can be conducted on a gram scale with excellent efficiency, demonstrating the practical application in future industry. Comparing to the previous report on the related selenocyclization reaction of alkynoates and alkynamides by Zeni's^{17e} and Liu's⁴⁹ work, this strategy requires no transition metals or chemical oxidants. Cyclic voltammetric (CV) experiments show that diphenyl diselenide had a lower oxidative potential than the substrate, indicating that diphenyl diselenide is more easily electrochemically oxidized to generate phenylselenium radical than the alkyne moiety.

Based on control experiments and radical quenching experiments, they proposed a possible reaction mechanism (Scheme 29). Diphenyl diselenide initially undergoes anodic oxidation to generate cationic radical intermediate **91**, which is decomposed to give phenylselenium radical **92** and phenyl selenium cation **93**. Thereafter, the radical addition of **92** to triple bond provides vinyl radical **94** in high regioselectivity. The resulting radical **94** participated in an intramolecular radical reaction to generate intermediate **95**, which is further oxidized on anode to afford the cation **96**. At last, deprotonation affords the final product **90**.

Inspired by this protocol, the group of Guo further developed the electrocatalytic oxidative radical dearomative spirocyclization for the preparation of selenation spiro[4.5]trienones **98** from alkynes **97** with diselenides (Scheme 30).³⁷ As mentioned above, when the substrates are alkynoates and alkynamides bearing a methoxy group at *para* substituted of aryl ring, the *ipso*-cyclization was occurred. Then, they optimized the reaction condition; the reaction worked well in CH₃CN/ HFIP (v:v = 3:1) at room temperature with *n*Bu₄NPF₆ as electrolyte. The use of the optimized reaction parameters led to the corresponding 49 examples of selenation spiro[4.5]trien-



Scheme 29 Proposed mechanism of electrochemically induced synthesis of selenated coumarins and quinolinones.



Scheme 30 Electrochemically induced synthesis of selenated spiro[4.5] trienones.

ones in moderate to good yields with broad substrate scope and high functional group tolerance. It is note that diphenyl ditelluride was also compatible for this transformation, giving tellurium-substituted products in good yields. It should be mentioned that terminal alkyne was not suitable for this system.

Notably, scale-up reaction was performed in electrochemical continuous flow system, and nearly the same yield was obtained (73% yield in nearly 15 h on the 10 mmol scale).

The authors also provided the possible mechanism (Scheme 31). Vinyl radical **99** is generated in the similar path and then undergoes intramolecular spirocyclization to provide **100**, different from their earlier work. Meanwhile, the anodic oxidation of the intermediate **100** generates oxygenium cation intermediate **102**. Finally, the sequential the demethylation of cation **102** and the dearomatization of the aromatic ring give access to the desired product.

In 2019, Pan and co-workers reported the electrochemical selenocyclization of olefins and diselenides for the generation



Scheme 31 Proposed mechanism of electrochemically induced synthesis of selenation spiro[4.5]trienones.



Scheme 32 Electrochemically induced synthesis of selenomethyl-substituted cyclic ethers, lactones and isobenzofuranones.

selenomethyl-substituted cyclic ethers or lactones of (Scheme 32).³⁸ The olefines including unsaturated alcohols and unsaturated carboxylic acids 103, were all suitable for this reaction with NH₄I as electrolyte and electrocatalyst, affording the corresponding products 104 in good yields. Moreover, the difficult-to-synthesize medium-sized ethers (7-, 9-, and 11-membered rings) and 4-6-membered ring lactones could be obtained smoothly. However, the reaction was limited to diphenyl diselenides bearing electron-donating groups (OMe), failing to produce the desired product with 2-vinylbenzoic acid. According to the results of cyclic voltammetry studies and control experiments, the reaction mechanism is depicted in Scheme 32. Iodine ion is first oxidized at anode to produce I⁺, which then reacts with olefnic alcohols to form iodonium cations intermediate 105. Subsequently, intramolecular cyclization and deprotonation lead to intermediate 106. Finally, rapid chemical selenation by diphenyl diselenide gives access to the desired product and a half molar equivalent of I2. At the cathode, reduction of I2 and proton to iodine anion and hydrogen completes the reaction cycle.

Dihydrofurans and oxazolines play important roles in numerous biologically active molecules, pharmaceuticals and agronomicals. As a straightforward and highly atom-economic method for synthesizing these derivatives, the selenocylization of olefinic carbonyls has attracted the attention of chemists. In 2019, the group of Lei realized an electrochemical oxidative cyclization between olefinic carbonyls and diaryl diselenides, providing a practical and enconomical approach to the preparation of selenium-functionalized dihydrofurans (Scheme 33).³⁹ This reaction could proceed smoothly in CH_3CN at room temperature with nBu_4NBF_4 as electrolytes, HOAc as additive, graphite as the working anode, and plati-



Scheme 33 Electrochemically induced synthesis of selenylated dihydrofurans and oxazolines.

num as the cathode. This method shows good compatibility for symmetric and unsymmetric olefinic carbonyls **107** with different substituents, giving the corresponding dihydrofurans compounds **108** in moderate to good yields. In addition, this protocol also tolerated unsaturated amides **109**, affording the corresponding seleno oxazolines **110** in moderate to excellent yields.

To gain more insight into this cascade cyclization, they added stoichiometric radical inhibitor TEMPO to reaction systems and perform this reaction under standard conditions. The yield of the desired product decreased obviously, indicating that the process involves a free radical pathway. Based on mechanistic studies, cyclic voltammetry studies, and the literature, the authors proposed two possible reaction pathways (Scheme 34). In path a, the anion radical intermediate 91 is generated by cathode reduction, and then decomposes to give phenylselenium radical 92 and phenyl selenium anion 93. Then, the radical addition of phenylselenium radical 92 to the alkene results in the formation of C-radical intermediate 111, which is further oxidized at anode. Finally, an intramolecular cyclization is occurred by nucleophilic attack of the oxygen atom of carbonyl, subsequent deprotonation to render the final product 108. In path b, the phenylselenium radical is generated by phenyl diselenide anode oxidation and decomposition.

The group of Sarkar reported the similar method for the electrochemical oxidative cyclization of *N*-allyl amides **112** and diaryl diselenides, providing a practical and flexible approach



Scheme 34 Proposed mechanism of electrochemically induced synthesis of selenylated dihydrofurans and oxazolines.



Scheme 35 Electrochemically induced synthesis of selenylated oxazolines and isoxazolines.

for the preparation of selenium-functionalized oxazolines **113** (Scheme 35).⁴⁰ The reaction could proceed smoothly in CH₃CN at room temperature with LiClO₄ as electrolytes, and graphite and platinum as the working anode and cathode, respectively. A variety of substituents on both electronic and steric effects can tolerate the oxidative conditions well. Moreover, amides with varying chain length were also compatible in the oxidative cyclization process. Notably, the thiazoline derivative was synthesized from corresponding *N*-allylthiobenzamide **113d**. Comparing to the Lei's work,³⁹ this method could also be suitable for β , γ -unsaturated oximes **114** and various isoxazolines **115** were achieved under the standard reaction conditions.

A plausible mechanism for this reaction was proposed based on mechanistic studies, cyclic voltammetry studies, and the literature (Scheme 36). In this mechanism, diphenyl diselenide is oxidized to generate cationic radical intermediate,



Scheme 36 Proposed mechanism of electrochemically induced synthesis of selenylated oxazolines and isoxazolines.

which is then decomposed to give phenyl selenium cation 93 and phenylselenium radical 92. Further oxidation of phenylselenium radical 92 leads to phenyl selenium cation 93. Subsequently, the addition of phenyl selenium cation 93 to alkenes 112 affords the cyclic seleniranium ion 116, which then is captured by the nucleophile amide oxygen to afford the final product 113. At the cathode, proton is reduced to the hydrogen, completing the reaction cycle.

Very recently, Ackermann and coworkers investigated an electrochemical oxidative cyclization of quinones and diaryl diselenides using a platinum plate anode and cathode under the constant current (10 mA) in an undivided cell (Scheme 37).⁴¹ Using lapachol 117, the quinone-hybrid compounds 118 were afforded with moderate to high yield *via* 6-*endo-trig* way. When this selenylation method was applied to the *C*-allyl lawsone 121, 5-*exo-dig* cyclization occurred to give the corresponding products 122 in good to moderate yields. Unlike a previous report in which a I₂/DMSO oxidant system was employed,⁴² this electrochemical reaction was conducted at room temperature without chemical oxidants. Moreover, some products exhibited considerable antitumor activity, indicating the promising in the application prospects.

3.4. I₂ and hypervalent iodine-catalyzed selenocyclization

3.4.1 I₂ catalyzed selenocyclization. In 2013, Braga's group reported the synthesis of seleno O-heterocycle using molecular iodine as catalyst, DMSO as a stoichiometric oxidant under microwave irradiation without solvent (Scheme 38).⁴² When using 4-penten-1-ol 123 or 4-pentenoic acid 125 as a substrate, the seleno tetrahydrofuran 124 or seleno-lactone 126 was obtained in excellent yield *via* the 5-*exo-trig* pathway. Moreover, lapachol 117 or *C*-allyl lawsone 121 was also suitable for this transformation, affording the corresponding product in good to high yields. However, nor-lapachol failed in this reaction. A plausible mechanism is proposed in Scheme 30. Initially, RSeI generated through the reaction of diorganyl diselenide with I₂ reacts with alkene to form seleniranium ion 127 and HI. Subsequently, intramolecular nucleophilic attack of the oxygen



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Scheme 38 $\,$ I_2/DMSO catalyzed synthesis of seleno tetrahydrofuran and seleno-lactone.

atom from the ester moiety on the carbon centre generates the final products. At the same time, HI is oxidized by DMSO to regenerate I_2 .

In 2019, Koketsu and co-workers reported an iodine mediated selenocyclization of 2-phenylalkynylquinoline-3-carboxylate **130** with diorganyl diselenides to access seleno pyrano[4,3-*b*]quinolin-1-one **131** (Scheme 39).⁴³ The reaction featured a wide range of functional group tolerances, including strong/weak electron-withdrawing/donating groups along with alkyl and aryl groups, affording the corresponding products in high yields. The possible mechanism proposed by the authors



Scheme 39 I_2 mediated synthesis of seleno pyrano[4,3-b]quinoline-1-one.

is disclosed in Scheme 39. R–Se–I to is generated *in situ* by the reaction of I_2 and (R–Se)₂. The electrophilic addition of R–Se–I to compound **130** forms seleniranium ion **132**. The intramolecular nucleophilic attack by O atom gives the intermediate **133**. Finally, the elimination of Me–I leads to target compounds. In a control experiment, MeI was detected based on NMR spectroscopy.

3.4.2 Iodine(m)-mediated selenocyclization. β,γ-Unsaturated hydrazones and oximes are valuable and versatile building blocks for preparation of pyrazoline and isoxazoline derivatives. In 2017, the group of Cai reported the cascade radical selenocyclization of β , γ -unsaturated hydrazones 134 via the oxidation of phenyliodine(m) diacetate, giving rise to the corresponding pyrazoline and isoxazoline derivatives 135 in good yields without any metal (Scheme 40).44 Due to the mild reaction conditions, this method had a wide tolerance for diorganyl diselenides. When a stoichiometric amount of TEMPO was added under standard conditions, the selenocyclization was completely suppressed, and the adduct was obtained in 84% yield. These results provide clear evidence that the process involves a C-centered radical intermediate formed by intramolecular cyclization. In these transformations, initially, the anionic intermediate is obtained by deprotonation of the β , γ -unsaturated tosyl hydrazone or oxime in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Subsequently, a SET process between intermediate 136 and PhI(OAc)₂ occurs to generate radical 137, which subsequently undergoes radical intramolecular cyclization to produce the C-centered radical 138. The diselenide then captures the C-centered radical 138, leading to the final product 135 and the phenylselenyl radical, which could recombine to diphenyl diselenide.

3.5 Peroxide-promoted selenocyclization

As an oxidant, Oxone[®] has been widely explored in organic synthesis due to its low cost, stability under various conditions, simple handling, and environmental nontoxicity. In 2019, Perin and coworkers described an efficient Oxone[®]-and dialkyl diselenides-promoted seleno-cyclization of 1,3-diynes **139** for the construction of diverse 5H-selenopheno[3,2-c]iso-



Scheme 40 Iodine(III)-mediated synthesis of β -selenyl pyrazoline and isoxazoline.



Scheme 41 Oxone® promoted synthesis of 5*H*-selenopheno[3,2-*c*] isochromen-5-ones.

chromen-5-ones **140** (Scheme 41).⁴⁵ This protocol enables the formation of four new chemical bonds, including one C–O bond and three C–Se bonds through a double intramolecular cyclization. Aryl-and alkyl-substituted 1,3-diynes were found to be suitable for this transformation. When $2\text{-CH}_3\text{OC}_6\text{H}_4$ -substituted 1,3-diyne was used as the substrate in the reaction, the yield of the target product was only 40% because of the competing reactions (intramolecular Se-cyclization and O-cyclization). A radical-trapping experiment using TEMPO and hydroquinone suggested this reaction does not involve a radical path. Furthermore, the ⁷⁷Se NMR experiment indicated that the active electrophilic selenium species are generated by the overoxidation of dibutyl diselenide by Oxone®.

Based on experimental findings, a plausible mechanism is proposed (Scheme 42). Firstly, the reaction of potassium peroxymonosulfate with diselenide affords two electrophilic selenium species ${}^{n}C_{4}H_{9}SeOSO_{3}^{-}$ (141) and ${}^{n}C_{4}H_{9}SeOH$ (142). ${}^{n}C_{4}H_{9}SeOH_{2}^{+}$ (145) is then formed by protonation of 142. Both electrophiles 141 and 145 can react with 1,3-diyne 139 to deliver the cyclic intermediate 146 *via* the elimination of HSO₄⁻ or water. Subsequently, the methyl group leaves under the attack of nucleophile to produce intermediate 149. Finally, the expected product 140 is afforded in the same way as above.

Subsequently, the authors further developed this methodology for the formation of 2,3-bis-organylselenylbenzo[*b*]chal-



Scheme 42 Proposed mechanism of Oxone® promoted synthesis of 5*H*-selenopheno[3,2-c]isochromen-5-ones.

cogenophenes (Scheme 43)⁴⁶ and 4-organoselanyl-1*H*-pyrazoles (Scheme 44)⁴⁷ by employing chalcogenoalkynes and α , β -alkynyl hydrazones as substrates by promotion of Oxone® and diselenides.

In 2019, the group of Baidya developed an efficient radical selenocyclization of *N*-aryl alkynamides **159** using $K_2S_2O_8$ as an oxidant in DCE at 80 °C (Scheme 45).⁴⁸ This method worked well in a switchable selectivity *ortho/ipso*-cyclization by



Scheme 43 Oxone® promoted synthesis of 2,3-bis-organylselenylbenzo[*b*]chalcogenophenes.



Scheme 44 Oxone® promoted synthesis of 4-organoselanyl-1*H*-pyrazoles.



Scheme 45 $K_2S_2O_8$ initiated synthesis of 3-selenyl quinolin-2-ones and 3-selenospiro[4,5]trienones.

Organic Chemistry Frontiers the change the substituent of N-aryl alkynamides 159, resulting in a variety of 3-selenyl quinolin-2-ones 160 and 3-selenospiro[4,5]trienones 161 in good to excellent yields. Moreover, diaryl diselenides and dialkyl diselenides were well tolerated in ortho cyclization. When propiolamides bearing para-fluoro and para-methoxy in the N-aryl ring were reacted with diaryl diselenides, the spiro-cyclic products were isolated in good to high vields. Alkyl-substituted propiolamides were also suitable for the ortho/ipso-cyclization. Radical trapping experiments by using TEMPO, butylated hydroxytoluene (BHT) or 1,1-diphenylethylene indicated that the process involves a free radical pathway. The authors carried out the reaction between 4-phenyl-quinolin-2-one and diphenyldiselenide under the standard reaction conditions and found that the selenylation process occurred before the ring-closure step. A tentative radical mechanism was depicted in Scheme 37. Initially, the K₂S₂O₈-mediated cleavage of the Se-Se bond of diselenide forms an aryl selenium radical, which undergoes a radical addition to N-aryl alkynamide and intramolecular spirocyclization to give radical intermediate 163. The intermediate 163 is oxidized to afford the intermediate 164, which is rapidly converted into the desired quinolone product 160 through 1,2-Cmigration and aromatization. When the N-aryl alkynamide bears para-F/OMe substituents, the intermediate 163 further reacts with solvated molecular oxygen to produce intermediate 166, which undergoes defluorination/demethoxylation via O-O

In 2019, Liu group reported the *tert*-butyl hydroperoxide (TBHP)-initiated radical cyclization of propargylic aryl ethers **167** with diaryl diselenides for the synthesis of diverse 3-organoselenyl-2*H*-coumarins **168** (Scheme 46).⁴⁹ The use of *N*-iodo-succinimid (NIS) could be *in situ* generation ArSeI with diaryl diselenides, increasing the reaction yield. For insight the mechanism, some control experiments were performed. TBHP was essential for this method, not only as radical initiator, but also with H₂O providing O atom proved *via* ¹⁸O-labeling experiment.

bond cleavage leading to the product 161.

According to the proposed mechanism (Scheme 47), aryl selenium radical and propargyl radical are generated *in situ* in the presence of TBHP as the oxidant and react with each other, leading to the key intermediate **170**, which was detected by GC. Aryl selenium radical then adds to alkyne triple bond **170** to produce the highly reactive alkenyl radical **171**. This radical undergoes intramolecular cyclization onto the phenyl moiety, giving intermediate **174**, which might be obtained by electrophilic cyclization of PhSeI in another path. Product **168** is gen-



Scheme 46 TBHP-initiated synthesis of 3-organoselenyl-2*H*-coumarins.



Scheme 47 Proposed mechanism TBHP-initiated synthesis of 3-organoselenyl-2*H*-coumarins.

erated by one of two pathways. In the first pathway, the solvent H_2O participates in the nucleophilic attack of **174** to generate an alcohol, which is further oxidized by TBHP to furnish **168**. In the second pathway, *tert*-butoxy radical gets an allylic hydrogen from **174** to generate radical intermediate **175**, which is subsequently trapped by the *tert*-butylperoxy radical to afford intermediate **176**. Finally, the cleavage of C–Se and O–O bonds intermediate **176** gives the targeted product **168**.

4. Conclusions

We have summarized recent advances in tandem selenocyclization and tellurocyclization between diselenides and alkenes or alkynes categorized by metal catalysis, visible-light catalysis, electrochemical catalysis, organocatalysis etc. Using such approaches, various important seleno-containing heterocycles can be efficiently accessed with high chemo- and regioselectivity and often with high atom economy. Additionally, the mechanistic features of these transformations have been discussed. The many successful examples presented in this review convincingly document the high potential of this approach in drug discovery, and some seleno-containing heterocycles have shown potent inhibitory activity against cancer cell growth. Despite the substantial advances in this area over the past few years, many challenges and problems remain to be solved. For instance, most of the tandem selenocyclization reactions discussed herein are based on two distinct reaction components. Reactions comprising three or even more components, which would further increase the structural space of the accessible compounds, are not well explored. Furthermore, designs for new diselenides should be developed. Asymmetric control also remains an important challenge. We hope that this review contributes to stimulating further advancement in the emerging research area of seleno cyclization reactions.

Conflicts of interest

There are no conflicts to declare.

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